

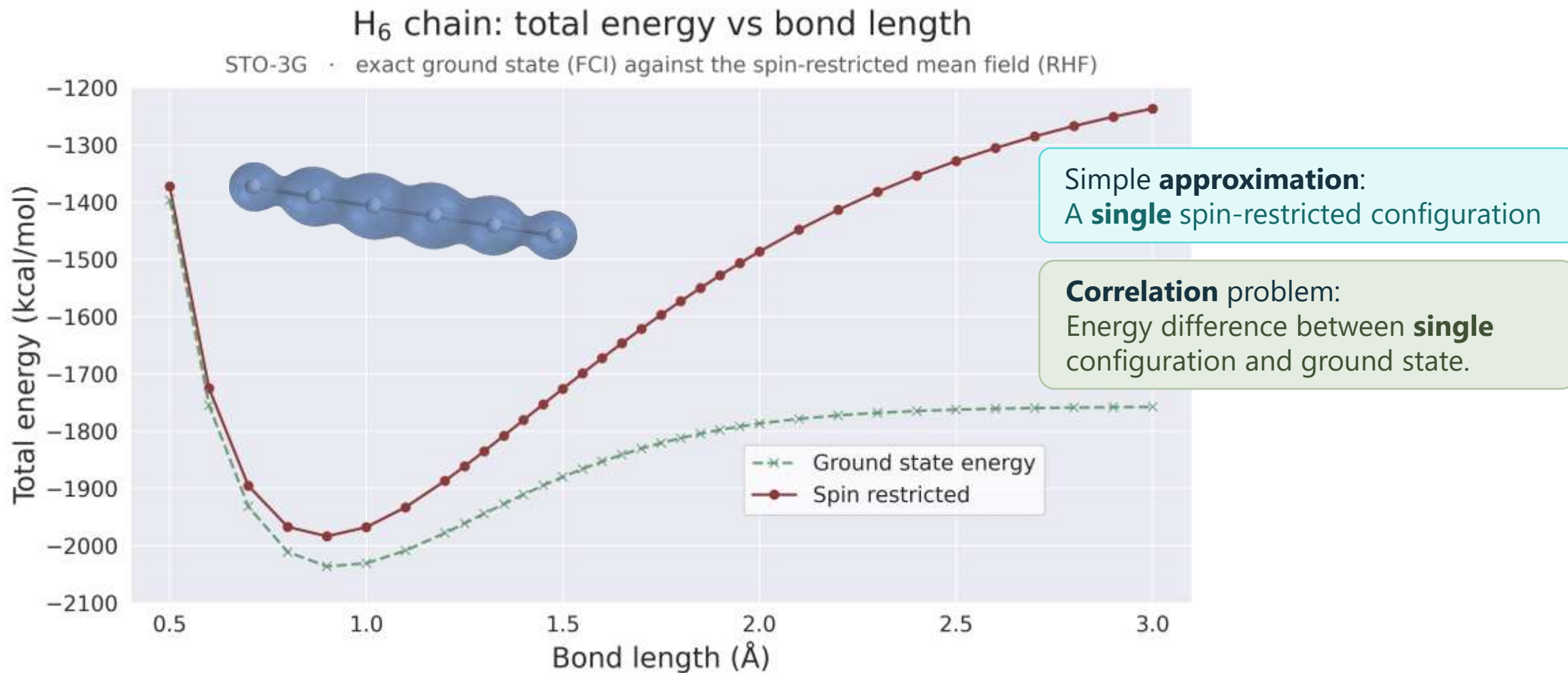
Breaking Ansatz Symmetry To Improve Sampling Efficiency

Freddie Burns · University of Bristol · 1st October 2026

Dr Hugh Burton · UCL

Prof Basile Curchod · University of Bristol

Motivation: Chemistry requires accurate binding curves.



Background: Energy levels are eigenvalues of Hamiltonian

Diagonalise (solve eigenvalues)

Number of basis functions scales **exponentially** with the number of electrons.

$$|\psi\rangle_0 = \sum_I c_I |\phi_I\rangle$$

$$\begin{array}{cccc} |\phi_0\rangle & |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle \\ \left[\begin{array}{cccc} H_{00} & H_{01} & H_{02} & H_{03} \\ H_{10} & H_{11} & H_{12} & H_{13} \\ H_{20} & H_{21} & H_{22} & H_{23} \\ H_{30} & H_{31} & H_{32} & H_{33} \end{array} \right] \end{array}$$

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$$\begin{array}{cccc} |\psi_0\rangle & |\psi_1\rangle & |\psi_2\rangle & |\psi_3\rangle \\ \left[\begin{array}{cccc} E_0 & 0 & 0 & 0 \\ 0 & E_1 & 0 & 0 \\ 0 & 0 & E_2 & 0 \\ 0 & 0 & 0 & E_3 \end{array} \right] \end{array}$$

Background: Diagonalising a subspace is quicker.

$$|\psi\rangle_0 = c_0|\phi_0\rangle + c_1|\phi_1\rangle + c_2|\phi_2\rangle + c_3|\phi_3\rangle$$

Support: subspace must include same basis as target eigenvector.

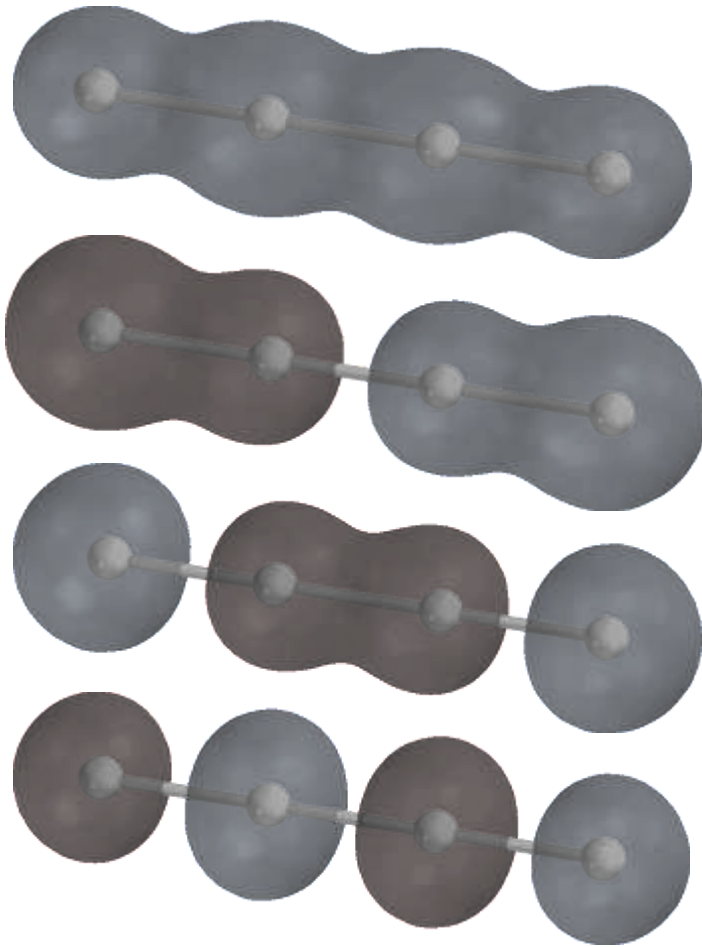
Variational: can't get energy lower than ground state energy.

Chemical accuracy = 1 kcal / mol

Say that $c_0 \ll c_1, c_2, c_3$

$ \phi_0\rangle$	$ \phi_1\rangle$	$ \phi_2\rangle$	$ \phi_3\rangle$
H_{00}	H_{01}	H_{02}	H_{03}
H_{10}	H_{11}	H_{12}	H_{13}
H_{20}	H_{21}	H_{22}	H_{23}
H_{30}	H_{31}	H_{32}	H_{33}

Background: The basis functions for the Hamiltonian are configurations of electrons among orbitals.



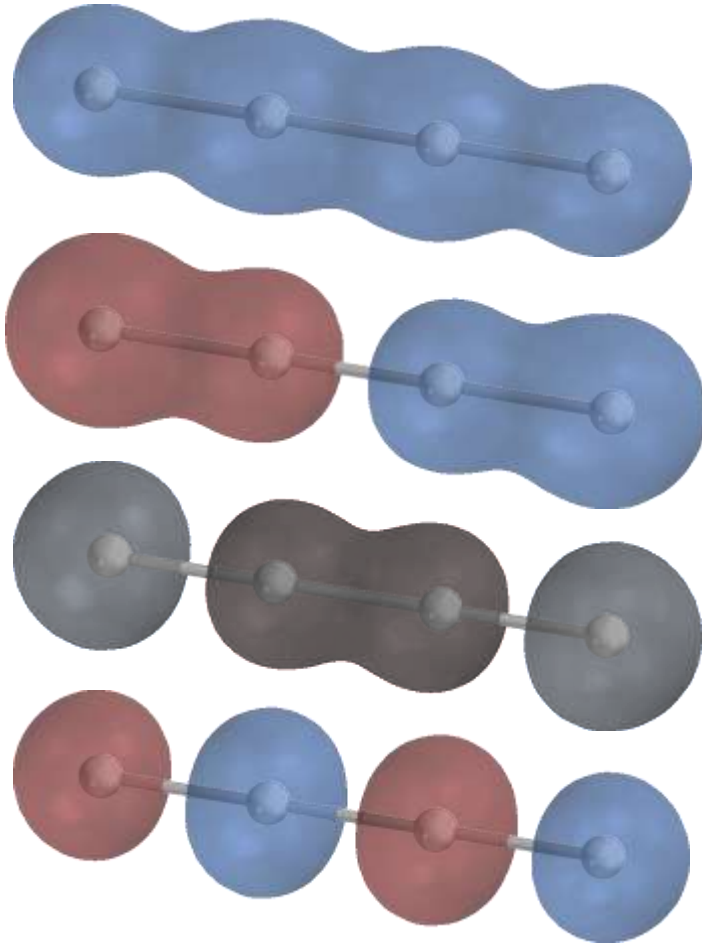
α

α

β

β

Background: The basis functions for the Hamiltonian are configurations of electrons among orbitals.



α

β

α

β

This **configuration** is written as:

$$|2\alpha 0\beta\rangle$$

or

$$|1100\rangle_{\alpha} |1001\rangle_{\beta}$$

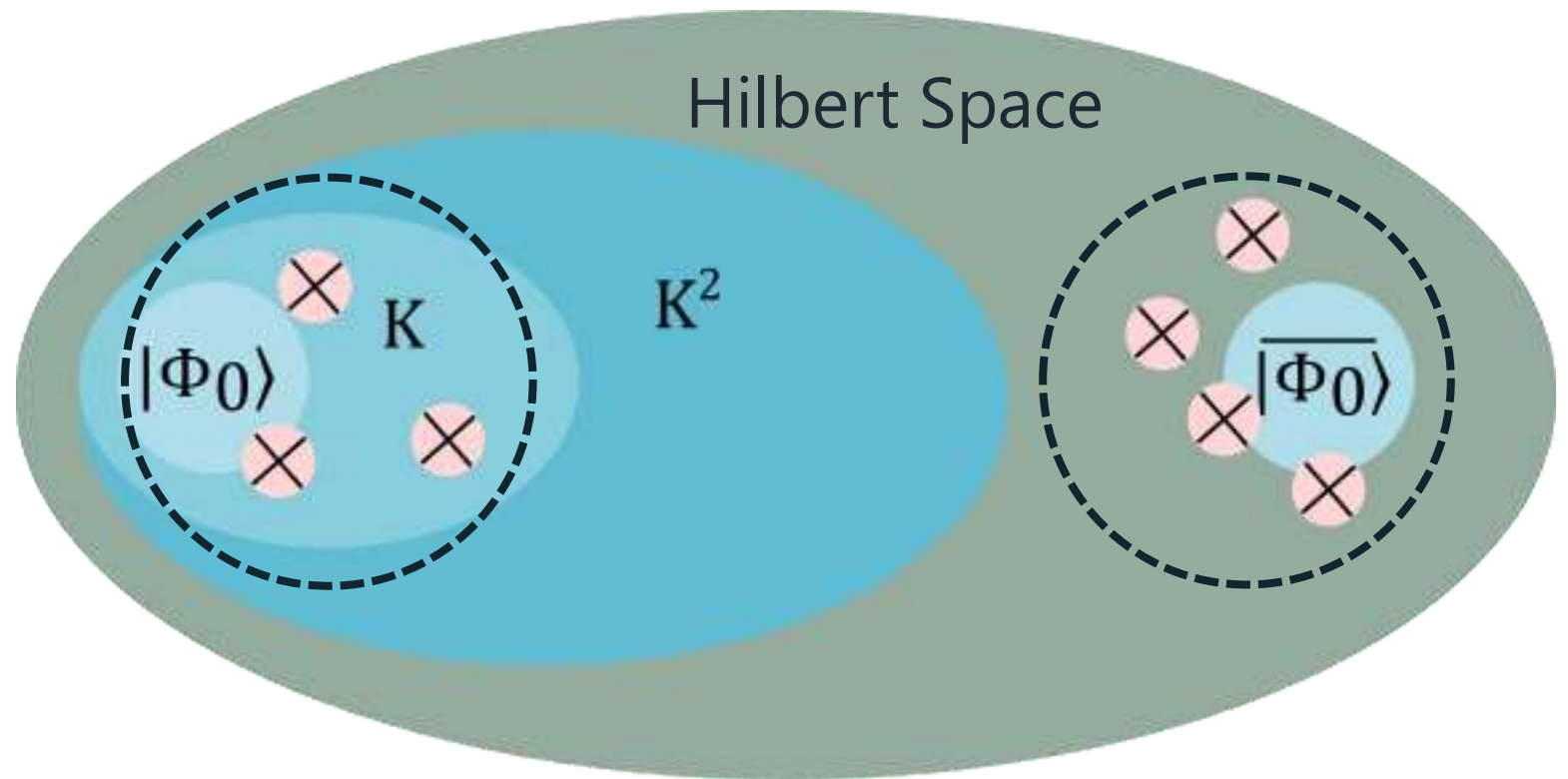
Motivation for Quantum: Ansatz can span Hilbert space at once

Classical methods build subspace from a reference $O(2^n)$. $\hat{K}$ is a permutation.

$$|\Phi_0\rangle = |\alpha\beta\alpha\beta\rangle$$
$$|\overline{\Phi_0}\rangle = |\beta\alpha\beta\alpha\rangle$$

Quantum sample
 $O(d \ln d)$

n = no. of orbitals
 d = support size



Which ansatz to use? The LUCJ is popular in the literature.

Local Unitary Cluster Jastrow - each layer is

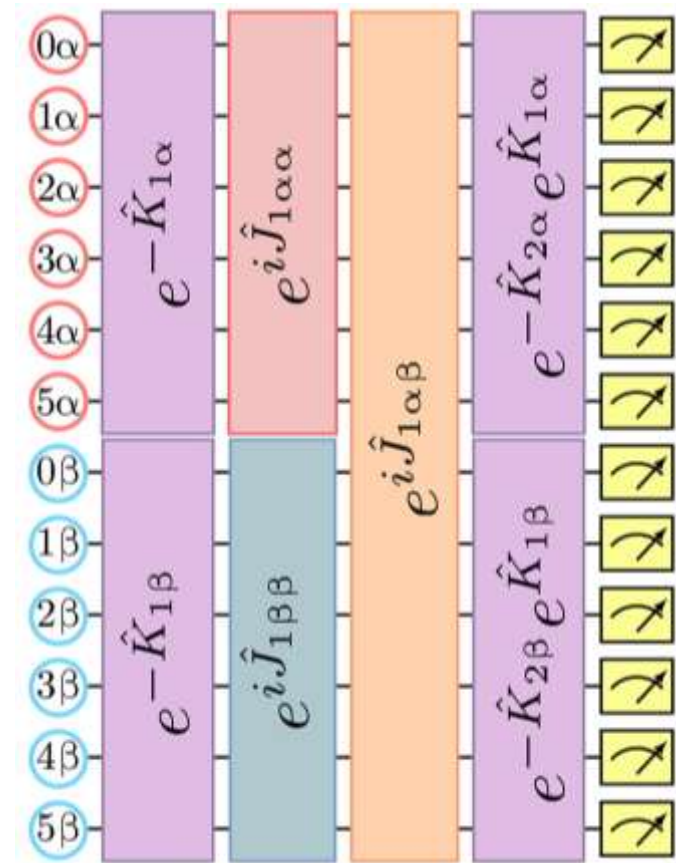
- **Basis** transformation
- "Jastrow" **correlation**
- **Basis** transformation

Parameters set by **classical** CCSD.

Approximates the **ground state**.

May **fail** where CCSD fails.

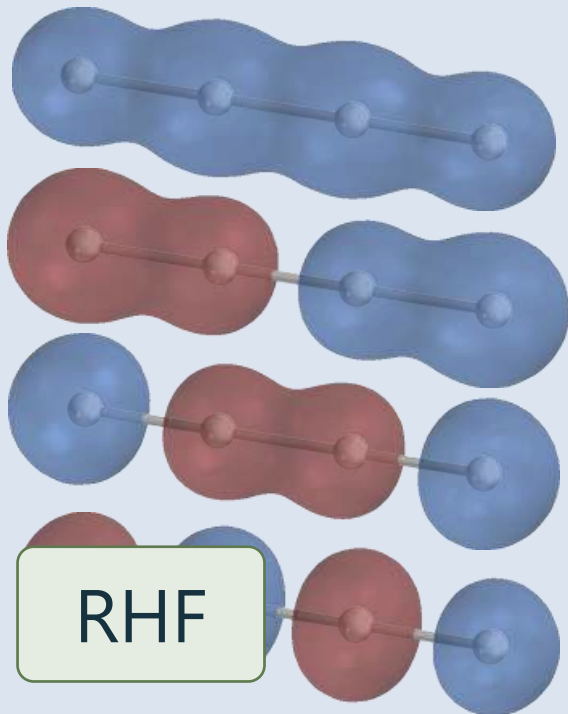
One LUCJ layer (6 orbitals)



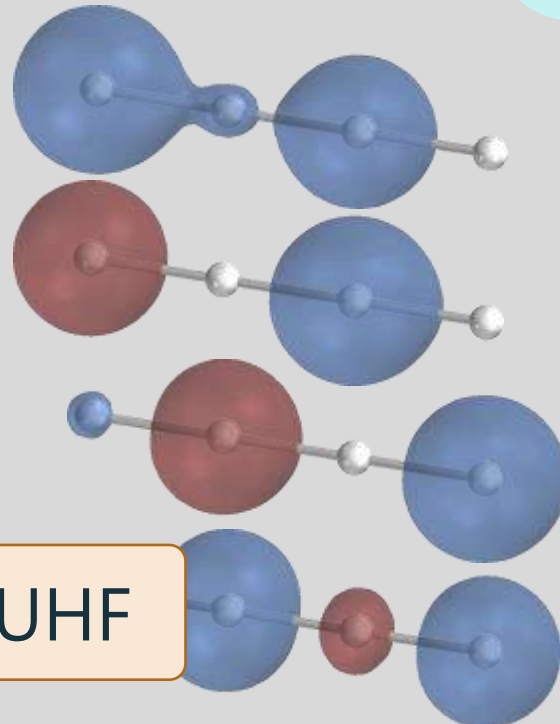
Usually, molecular orbitals are chosen to preserve total spin.
Removing this restriction = lower energy “spin-broken” orbitals.

$[\hat{H}, \hat{S}^2] = 0$ Energy eigenstate must be a spin eigenstate.

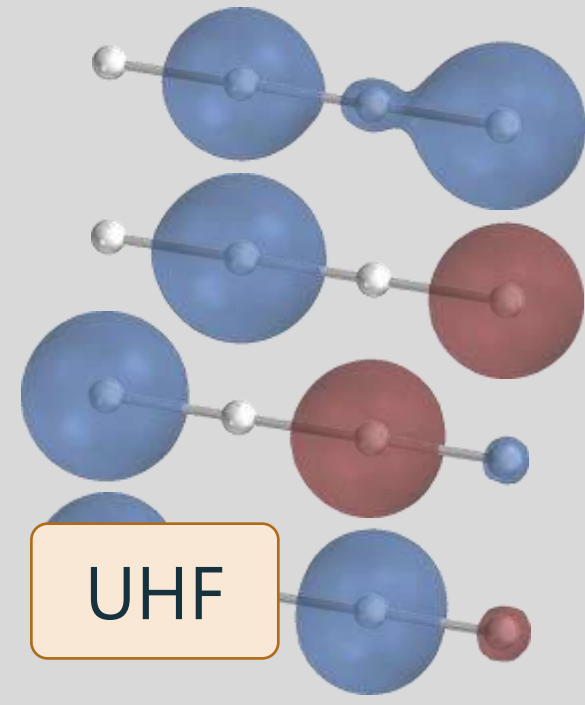
Spin restricted



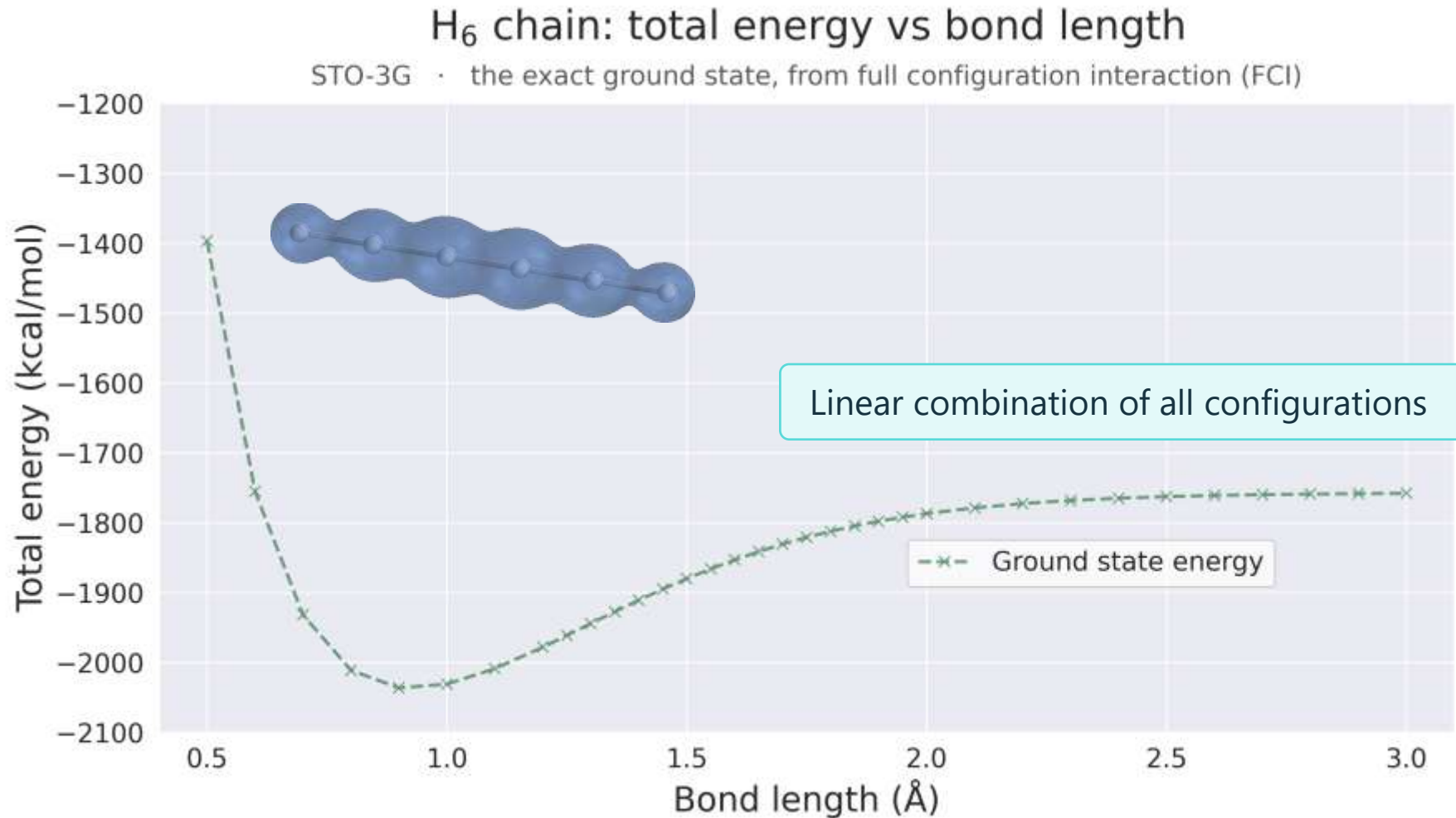
Spin broken α



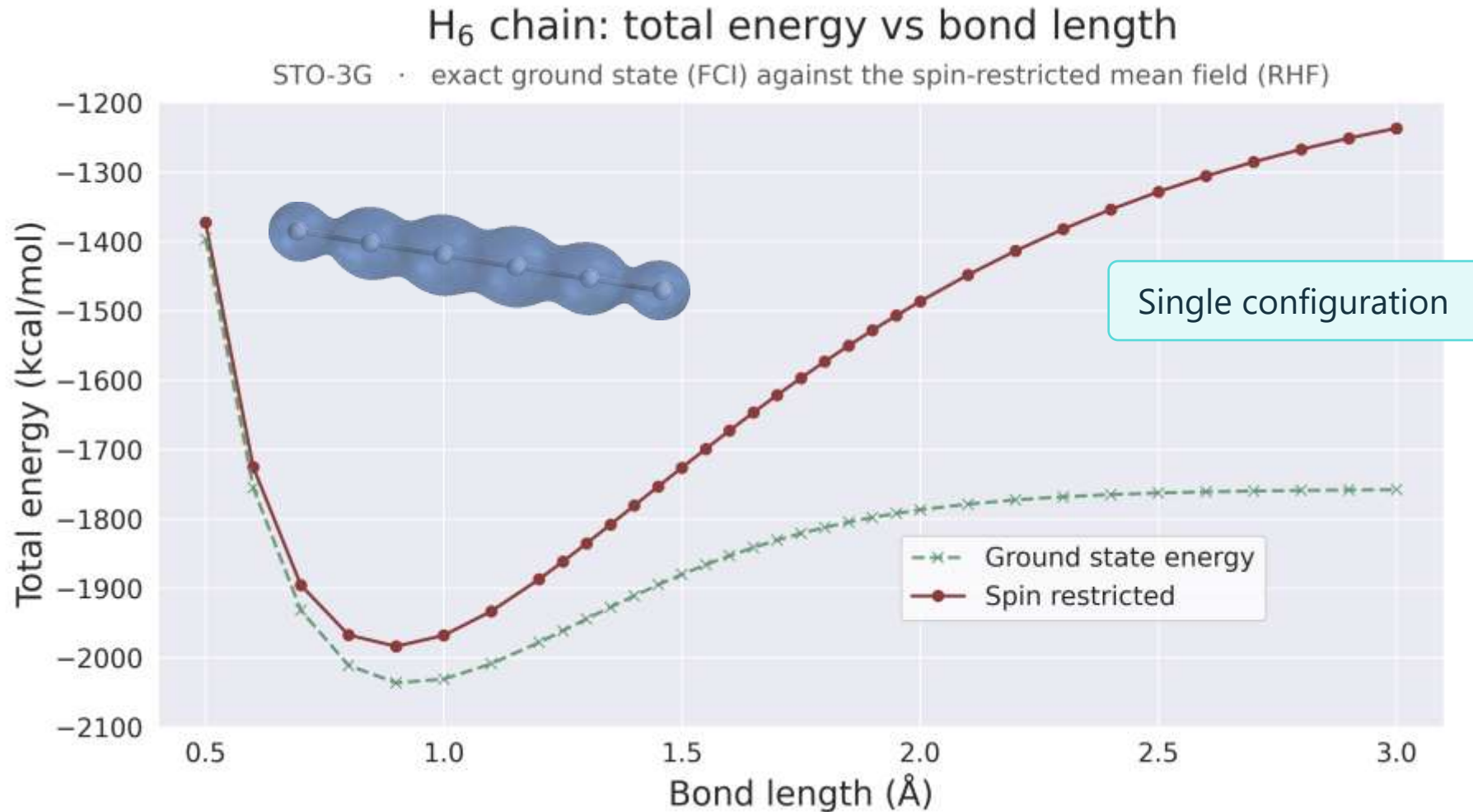
Spin broken β



Spin breaking can lower the energy of a configuration

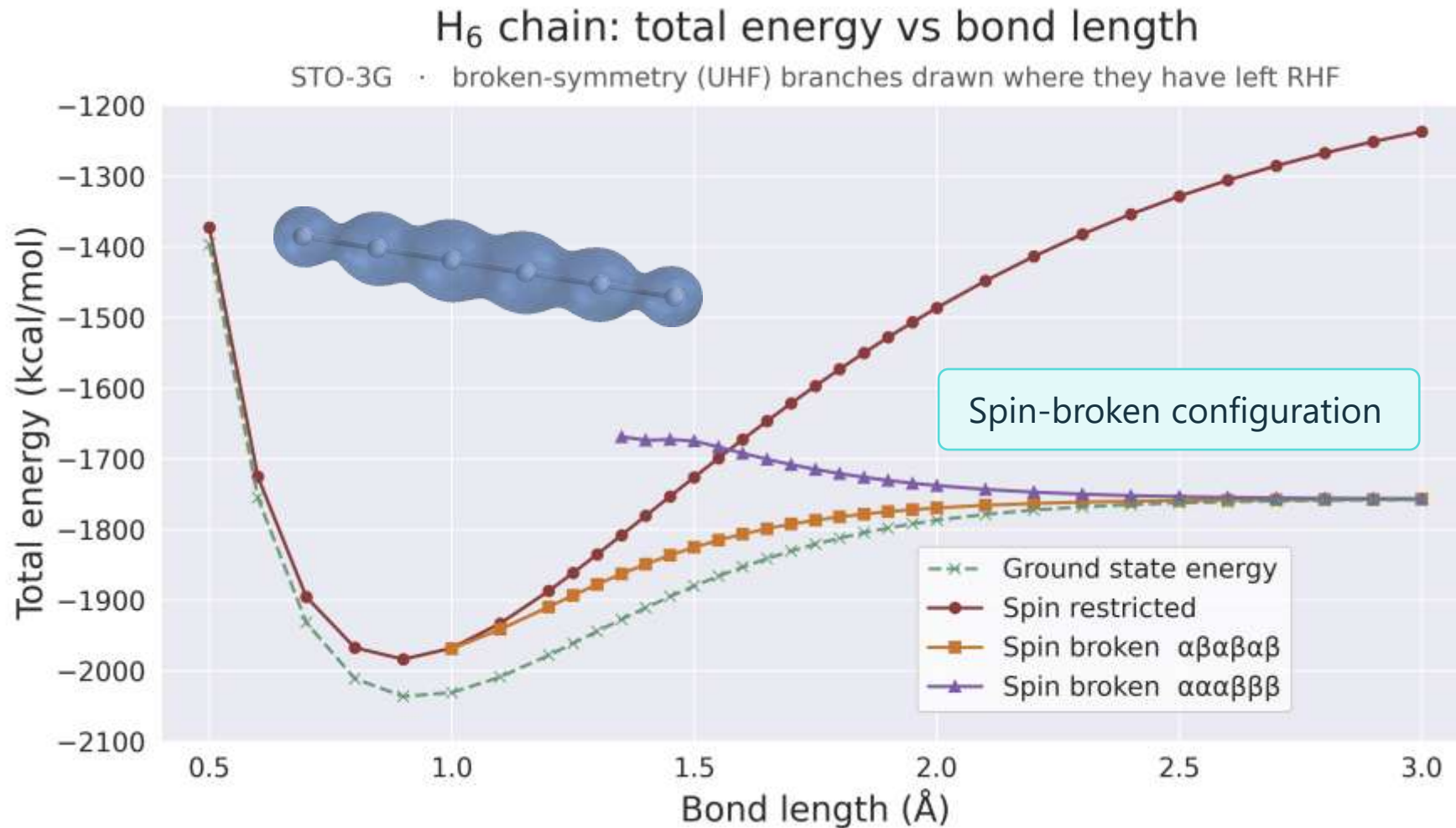


Spin breaking can lower the energy of a configuration



Coulson & Fischer, Phil. Mag. 40, 386 (1949))

Spin breaking can lower the energy of a configuration

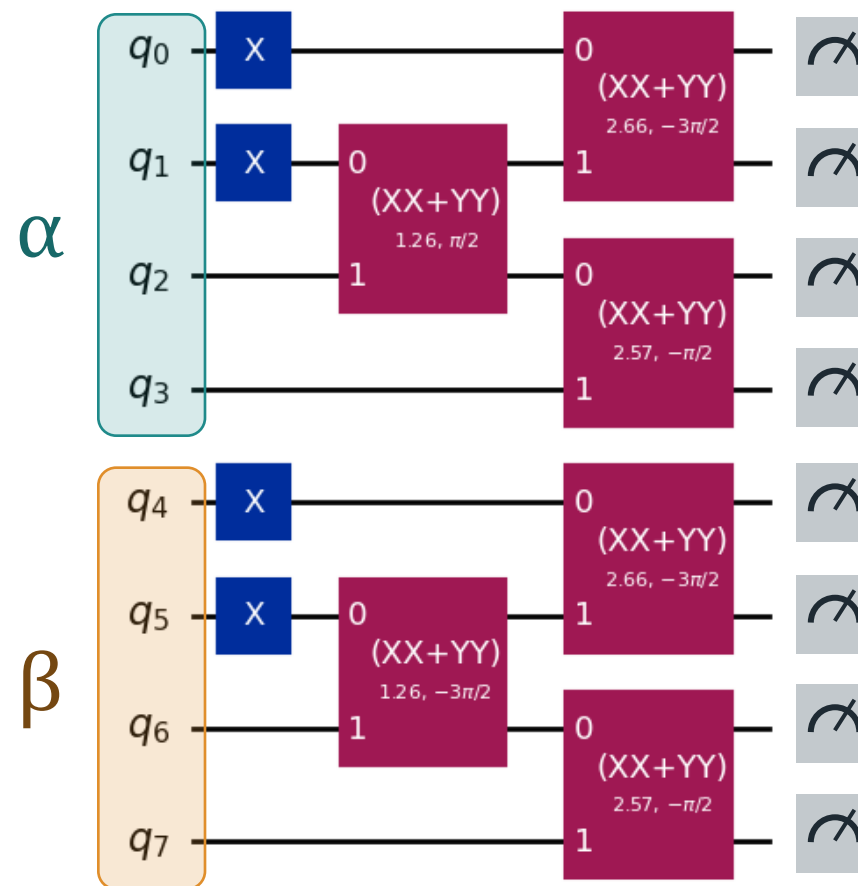


Coulson & Fischer, Phil. Mag. 40, 386 (1949) · Pople & Nesbet, J. Chem. Phys. 22, 571 (1954)

Our idea: Sample a low energy spin broken (UHF) configuration in a spin restricted (RHF) basis.

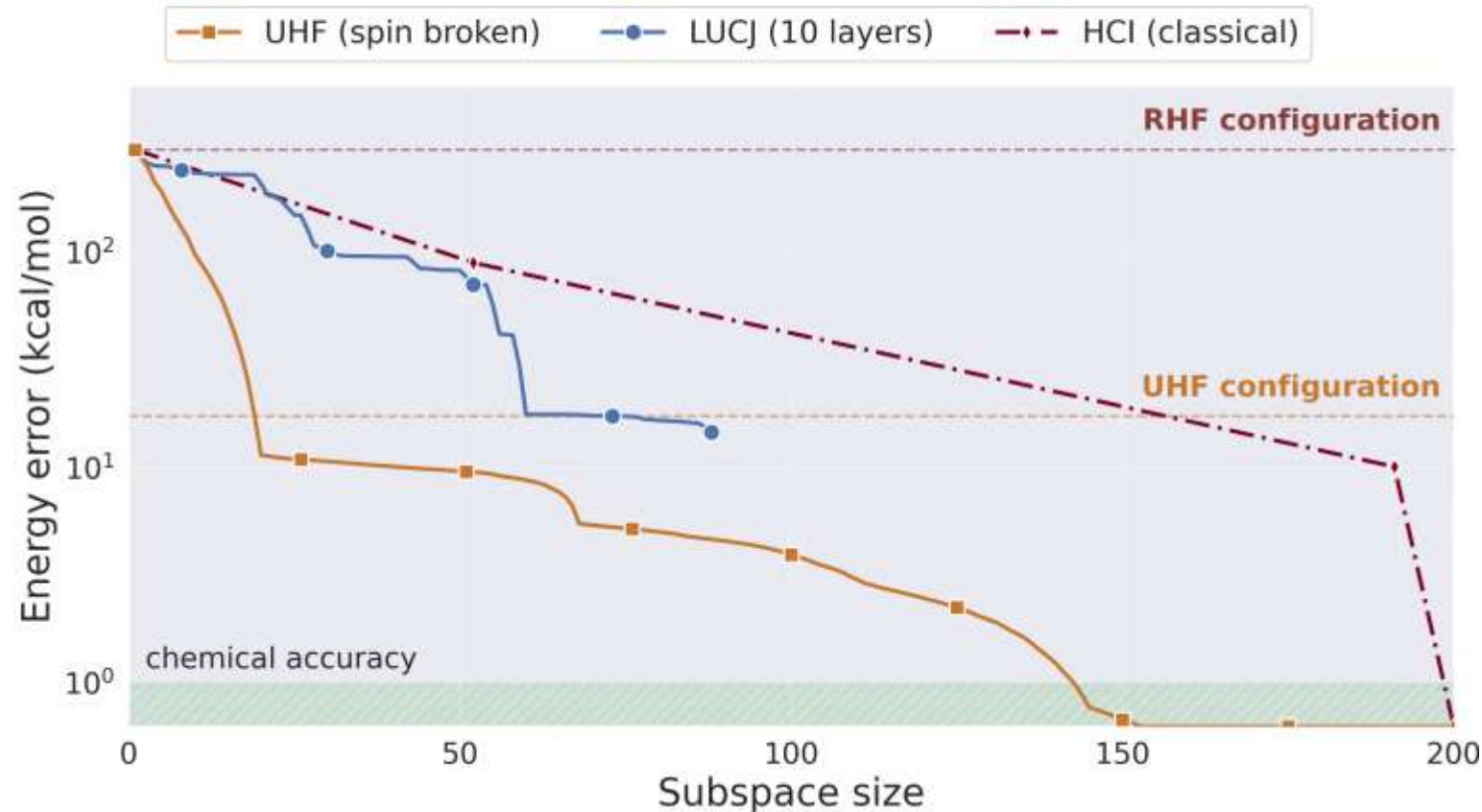
$$\begin{aligned} &|1100\rangle_{\alpha}|1100\rangle_{\beta_{\text{UHF}}} \\ &= c_0|1100\rangle_{\alpha}|1100\rangle_{\beta_{\text{RHF}}} \\ &+ c_1|1010\rangle_{\alpha}|1100\rangle_{\beta_{\text{RHF}}} \\ &+ c_2|1100\rangle_{\alpha}|1010\rangle_{\beta_{\text{RHF}}} \\ &+ c_3|1001\rangle_{\alpha}|1010\rangle_{\beta_{\text{RHF}}} + \dots \end{aligned}$$

The coefficients encode a **basis transformation** from unrestricted-spin to restricted-spin orbitals.



Simulation: We produce lower error than the LUCJ ansatz and smaller subspace than classical methods.

Energy error vs subspace size: H_6 at $2.0 \text{ \AA}$, 10^5 noiseless shots



UHF sampled in **RHF** basis

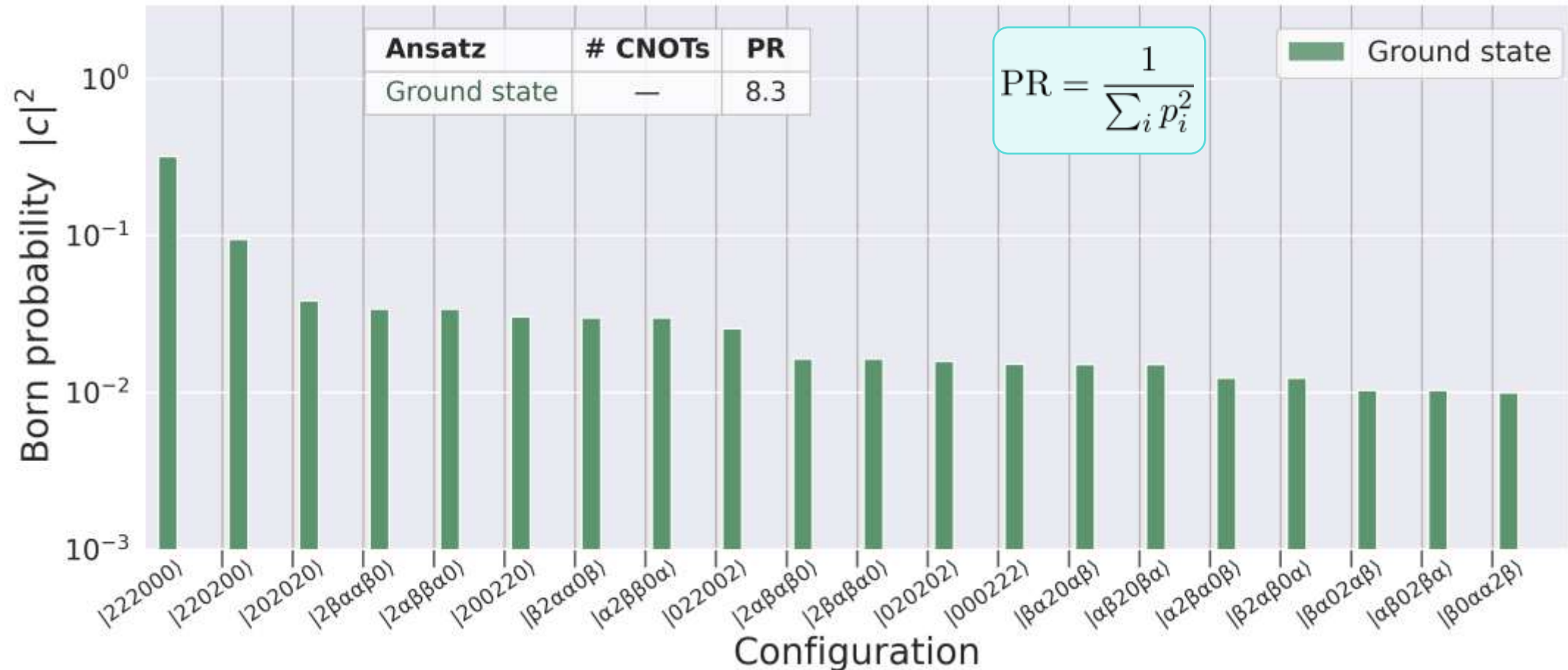
Reaches **chemical acc.**

Discovers more configurations than LUCJ

More compact subspace than classical HCl

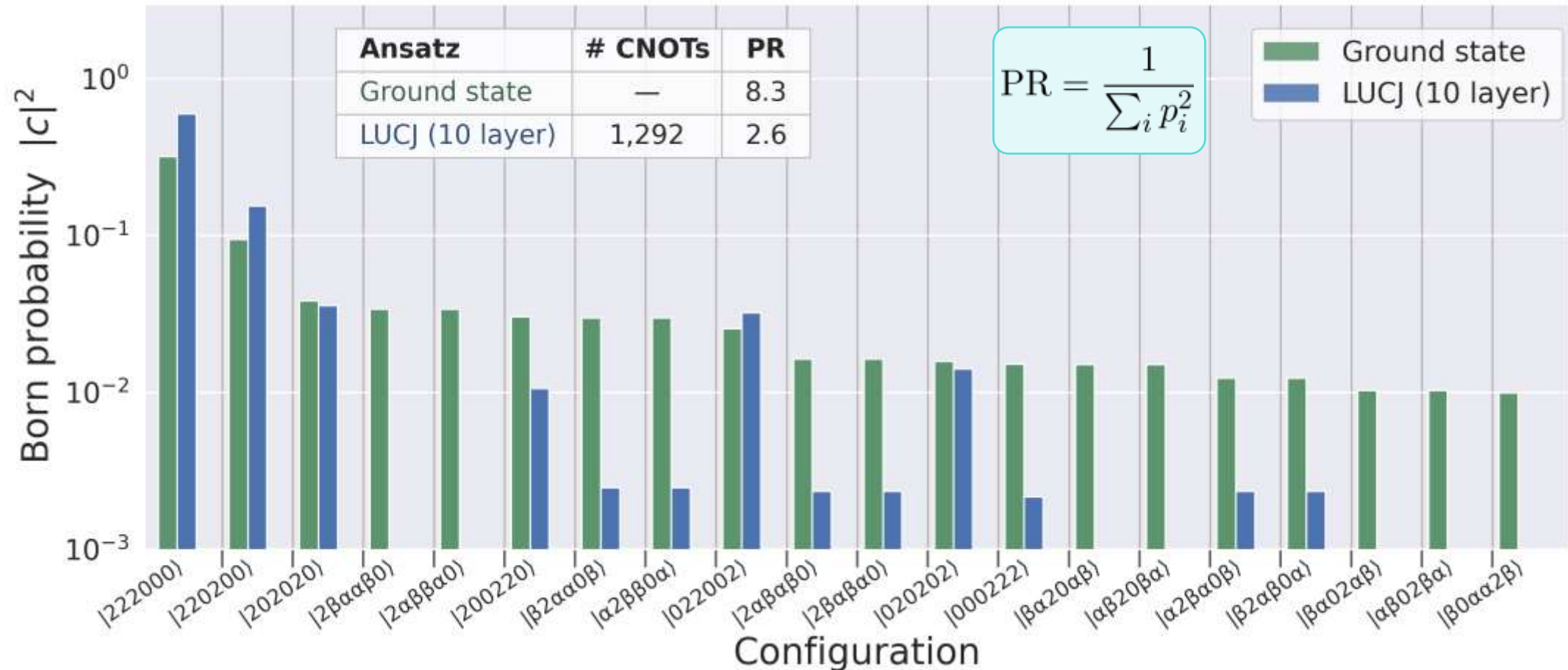
Simulation: Spin breaking makes sampling more efficient by flattening the probability distribution.

H₆ at 2.0 Å, STO-3G: weight on each of the top 20 configurations



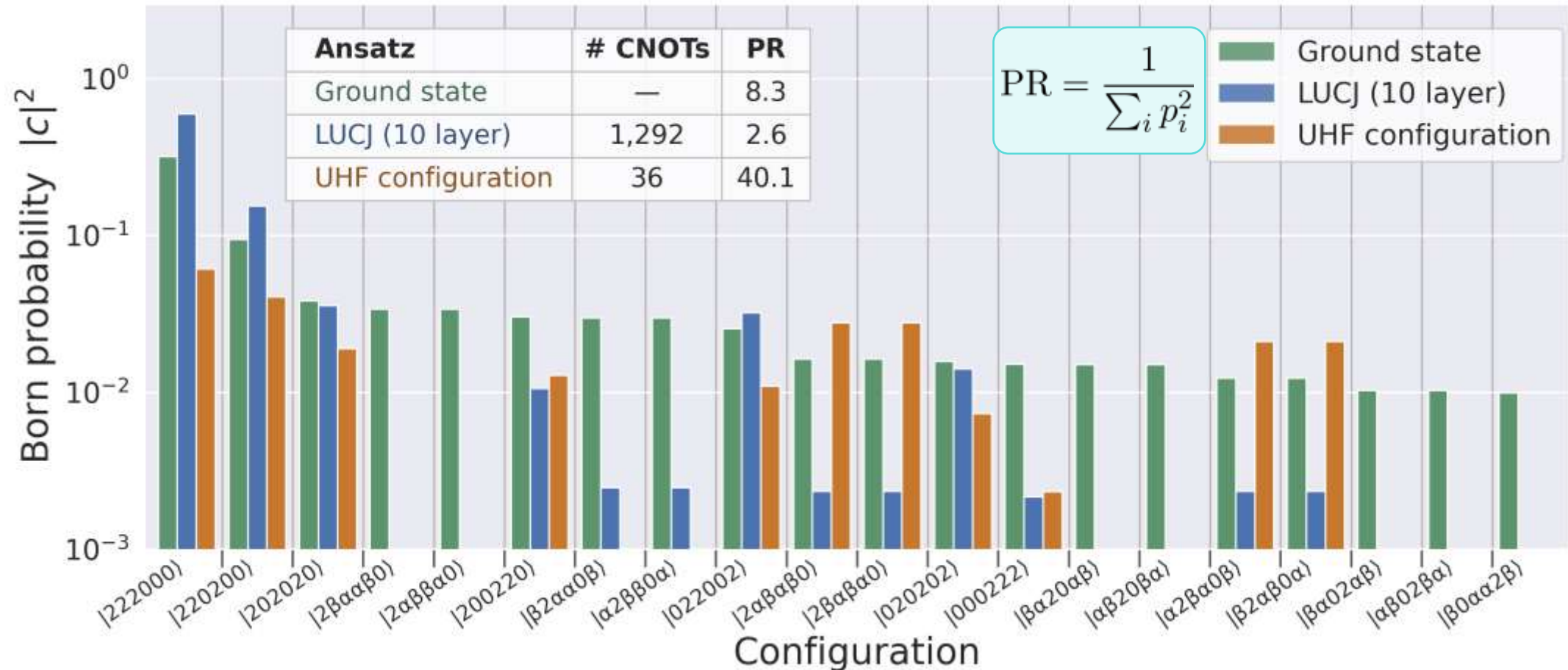
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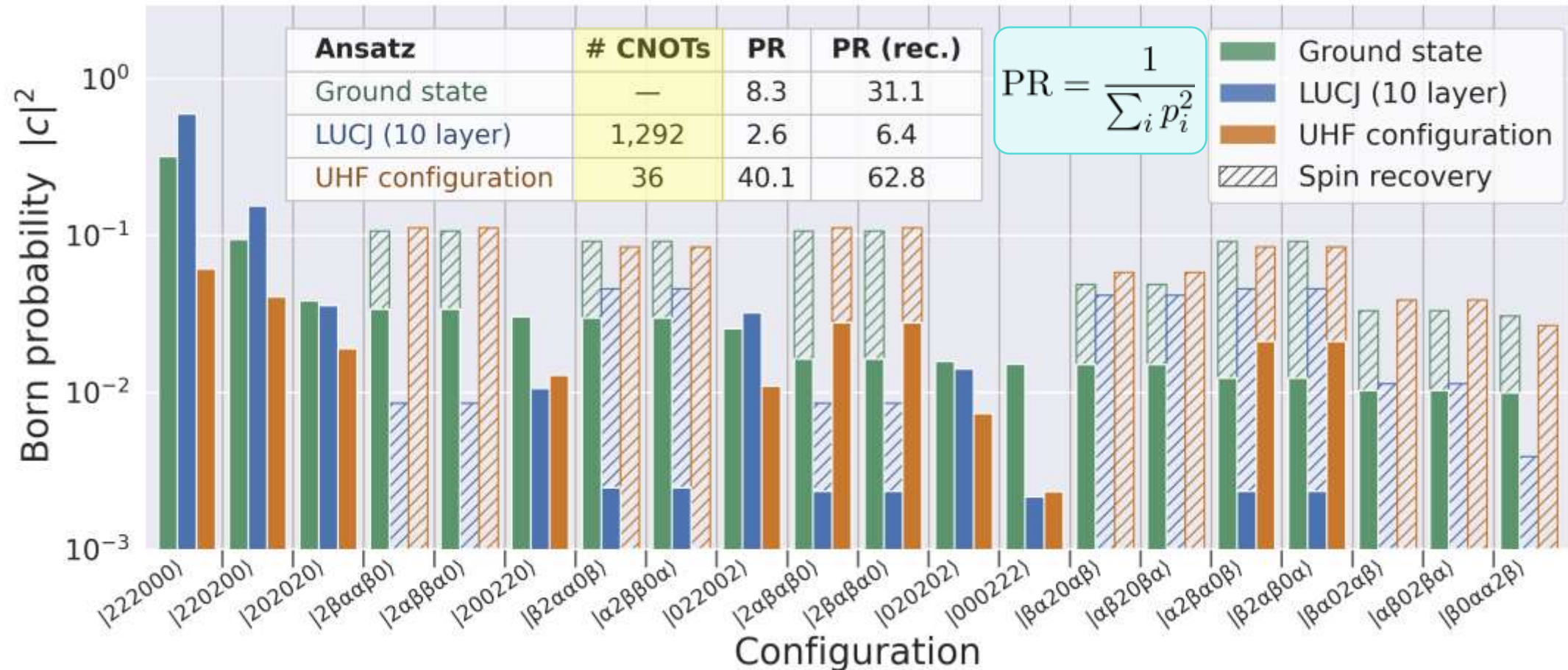
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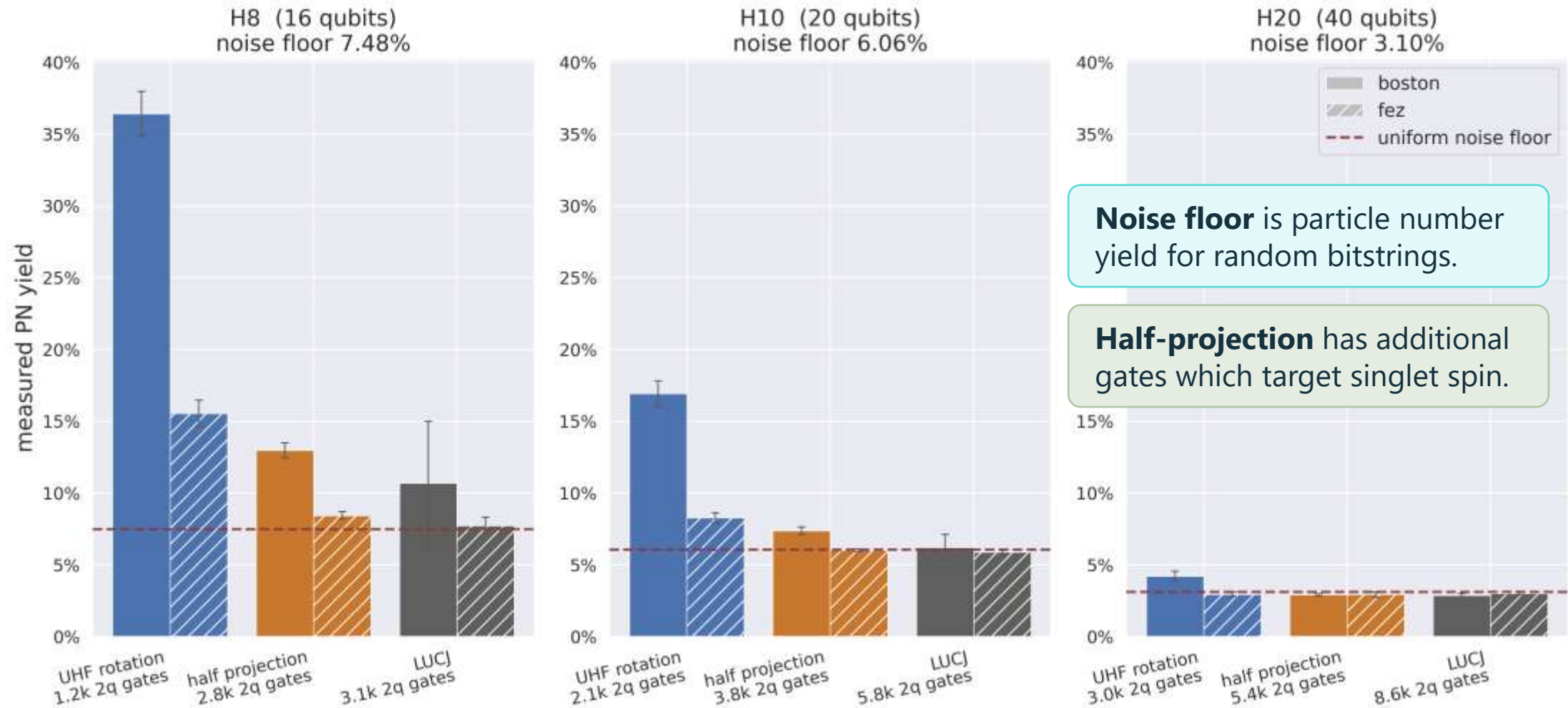
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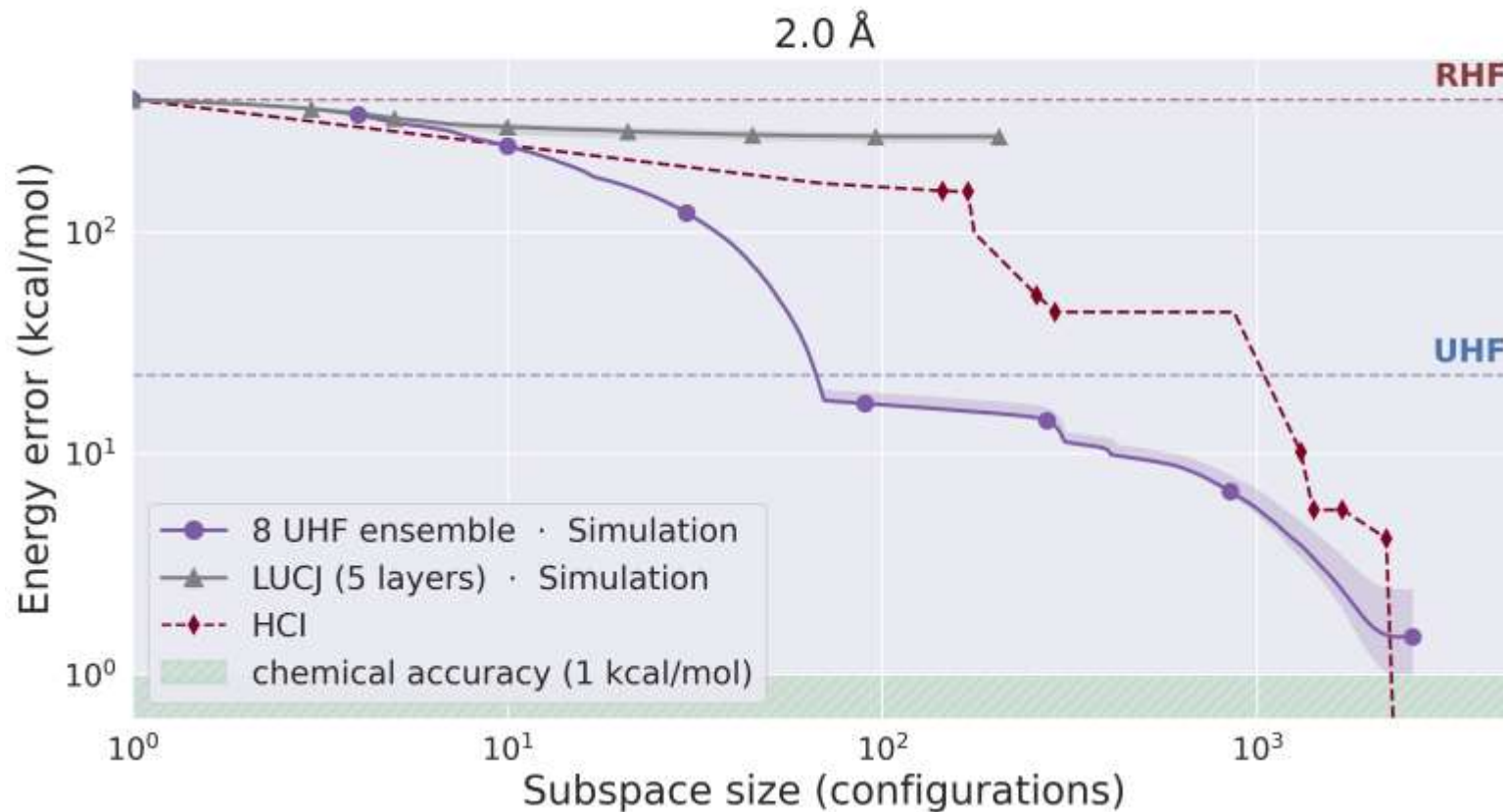
SparQ Results: Our shallower circuits reduce errors.

Percentage of measurements with correct number of electrons.



Simulation: Increasing system size reveals accuracy limits.

H₈ chain, STO-3G: QSCI energy at a 100k-shot budget



Ensemble of UHF circuits

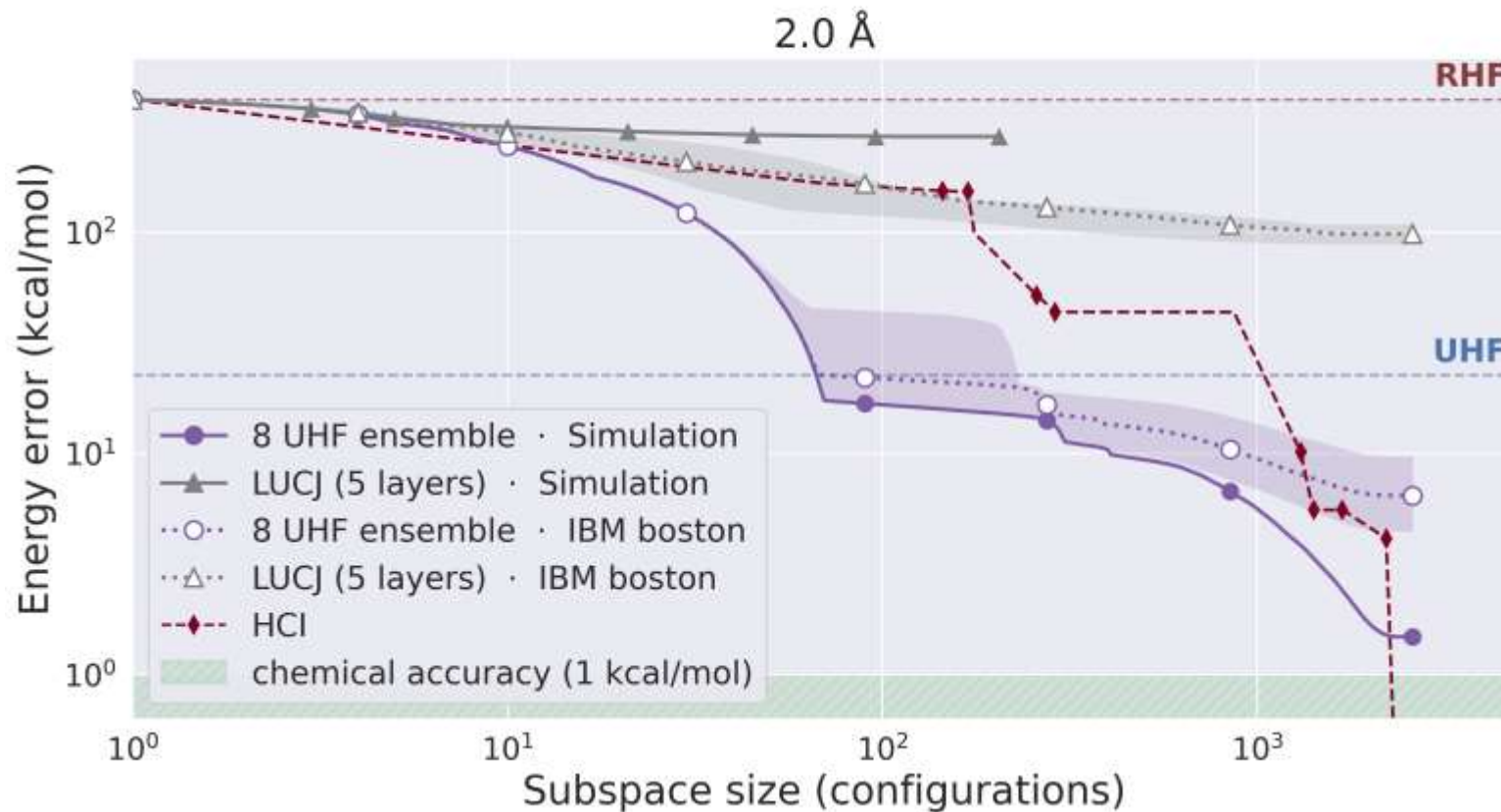
Lower error than LUCJ

Discovers more configurations than LUCJ

Does **not reach** chemical accuracy

SparQ Results: Increasing system size reveals accuracy limits.

H₈ chain, STO-3G: QSCI energy at a 100k-shot budget



IBM Boston hardware

Noise increases **UHF error**

Noise improves **LUCJ**

We are investigating **other UHF solutions**

Summary: H_6 chain reaches chemical accuracy with 4× fewer CNOTs than 1 LUCJ layer and 25% fewer configurations than HCl

Method

- 1 Find **spin-broken** molecular orbitals (UHF)
- 2 Sample a spin-broken determinant in a **spin-restricted** basis
- 3 Diagonalise the Hamiltonian in the **measured subspace**

Results on H_6 at 2.0 Å

36

CNOTs in the circuit,
against 144 for LUCJ layer

15×

flatter distribution (PR)
meaning **fewer shots**

150

configurations against
200 for classical HCl